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Oxygen Induced Surface Core Level Shifts of W(110) Deduced From Surface Segregation Energies

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Résumé. — Nous calculons le déplacement de niveau de cœur induit par la présence d'oxygène à la surface (110) d'un cristal de tungstène. Nous utilisons l'approximation de cœur équivalent, ce qui ramène le problème au calcul de la variation, due à la présence d'oxygène chimisorbé, de l'énergie de ségrégation d'une impureté de rhénium à la surface (110) d'un cristal de tungstène. On se place dans l'approximation des liaisons fortes. Les résultats sont comparés à d'anciens modèles moins élaborés et nous permettent de proposer une nouvelle interprétation des données expérimentales.

Abstract. — We calculate the core-level shift induced by oxygen adsorbates on the surface atoms of W(110). We use the equivalent core approximation which reduces this problem to the computation of the variation of the surface segregation energy of a rhenium impurity in a (110) tungsten crystal due to the presence of chemisorbed oxygen atoms. The calculation is carried out in the framework of the tight-binding approximation. The results are compared with previous simpler approaches and suggest a new interpretation of experimental data.

1. Introduction

It has been recognized, for thirty years, that the core-electron levels of an atom are very sensitive to its chemical and geometrical environment and are therefore a fine tool for determining the atomic structure [1]. Core electron binding energy shifts between surface and bulk atoms (SCLS) can be measured by high resolution photo-electron spectroscopy and their comparison with theoretical results allows us to check the validity of structural models.

Two kinds of models were proposed at the beginning of the 80's to calculate the SCLS : the microscopic model [2] and the thermodynamical model [3]. In the former, the SCLS is equal to the change of the core orbital eigenenergy before the excitation process, i e., the electronic

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relaxation energy, which follows the creation of the core hole, is assumed to be the same at the surface as in the bulk. In the latter, thermodynamical arguments using the equivalent core approximation show that the SCLS can be identified with the surface segregation energy of an impurity $[Z+1]$ in a $[Z]$ matrix (where $[Z]$ represents an element of atomic number Z). In this approach, the electronic relaxation contribution is taken into account. However, in a first theory [3] the surface segregation energy was replaced, for clean surfaces, by the difference of surface energy between the elements $[Z]$ and $[Z+1]$ by assuming that some dilution terms can be neglected.

Recently, Said *et al.* [4] have computed the segregation energy of a $[Z+1]$ impurity at the surface of a clean $[Z]$ matrix, using a tight-binding approach. Their results show that the dilution term, as well as the electronic relaxation contribution are not always negligible and this explains the discrepancy observed between experimental data and previous calculations for Ta(111). The same conclusion has been reached by Aldén *et al.* [5] from *ab initio* calculations of surface segregation energies on the most close-packed fcc, bcc and hcp transition metal surfaces. Here, we will adopt the same point of view to study the modification of the SCLS of W(110) due to chemisorbed oxygen atoms in the vicinity of the core-excited atom.

After briefly reviewing the different methods for computing the SCLS, we will describe the calculation of the surface segregation energy in the presence of an adsorbate. Then, we will consider two limiting cases: the case of a whole overlayer of oxygen and that of a very low oxygen coverage. We will compare our results with those of the microscopic and previous thermodynamical models, as well as with experiments.

2. Brief Review of Theoretical Approaches for the Calculation of the SCLS

Let us first recall the experimental process which is used to measure the SCLS: a core electron with an initial orbital eigenenergy E_c^{bulk} in the bulk (E_c^{surf} at the surface, respectively) is expelled from the solid by a photon of energy $h\nu$ and its final kinetic energy E_k^{bulk} (respectively E_k^{surf}) in vacuum is measured. The SCLS is indeed the difference $E_k^{\text{bulk}} - E_k^{\text{surf}}$.

2.1. MICROSCOPIC MODEL. — In this model, the SCLS between a surface atom and a bulk atom is split into two contributions

$$\Delta^{\text{SB}} = E_c^{\text{bulk}} - E_c^{\text{surf}} + \Delta_{\text{relax}}^{\text{SB}} \quad (1)$$

The first term is directly derived from the Koopmans theorem and the second accounts for the difference in readjustment of the valence charge between the surface and the bulk upon the creation of the hole in the final state [6]. If the screening of this hole is mainly due to fairly localized electrons, which is in particular the case for transition metals, we can, in a first approximation, neglect $\Delta_{\text{relax}}^{\text{SB}}$ since the electronic relaxation energy should not be too sensitive to the presence of the surface. Eventually, it can be argued from electrostatics that the displacements of the core levels follow almost rigidly the displacement of the valence d-levels. Thus:

$$\Delta^{\text{SB}} \simeq E_d^{\text{bulk}} - E_d^{\text{surf}} \quad (2)$$

In the tight-binding approximation, E_d^{bulk} (E_d^{surf}) is the center of gravity of the local d-density of states on the excited bulk (surface) atom. The quantity $E_d^{\text{bulk}} - E_d^{\text{surf}}$ is determined self-consistently by assuming the charge neutrality of each atom [2, 7].

Save for some peculiar cases, this model has been successful to explain or predict the SCLS at clean surfaces for 5d transition metals. It has also been applied to study the SCLS in the presence of chemisorbed atoms. The observed trends are correctly reproduced but quantitative

agreement between theory and experiments is, on the whole, less satisfactory than for clean surfaces.

2.2. THERMODYNAMICAL MODEL. — All thermodynamical models are based on the equivalent core approximation that we will first recall.

When a core-electron is expelled, the resulting electrostatic potential is screened in the final state by a valence electron. Since the overlap between the d valence electron orbitals and the core-electron orbitals is very small, the potential felt by these valence electrons is mainly determined by the net charge of the ion cores and thus is rather insensitive to their detailed charge distribution. Consequently a core ionized [Z] atom can be replaced with a good accuracy by the ion core of the element [Z+1]. Therefore the SCLS is equal to the surface segregation energy of a substitutional [Z+1] impurity in a metal of atomic number Z.

However, in the beginning of the eighties, no systematic data on these quantities were available in the literature, even in the case of clean surfaces. Thus Johansson and Mårtensson have built up a Born-Haber cycle in which the segregation energy for clean surfaces was split into two contributions [3]. The first one is the difference of surface energy between the elements [Z+1] and [Z] and the second one is a dilution term which was neglected by these authors. This model has been reasonably successful to explain the SCLS on clean surfaces.

This approach has been generalized for adsorbate covered surfaces and it was shown, using several approximations which have been discussed elsewhere [7], that the presence of chemisorbed atoms introduces an additional contribution to the SCLS given by

$$\Delta^{S'S} = -\frac{p'}{p}(E_{\text{ads}}(Z+1) - E_{\text{ads}}(Z)) \quad (3)$$

where $E_{\text{ads}}(Z)$ is the (positive) adsorption energy of the adatoms at the surface of the [Z] crystal (here the element [Z+1] is assumed to have the same crystalline structure as the element [Z]), p is the number of bonds (assumed to be geometrically equivalent) of an adatom with the substrate atoms and p' is the number of bonds (also assumed to be geometrically equivalent) between the substrate atom on which the SCLS is measured and the adsorbates. In the usual cases where these bonds are not equivalent, the above formula can still be used to get an average value of the additional SCLS due to adsorbate(s).

The agreement between this theory and experiments is most often only qualitative. In particular some problems arise when there exists inequivalent sites on the surface since at each geometrically inequivalent environment should correspond a different SCLS and this is the most commonly encountered case. An obvious way of improving this model is to avoid any approximation other than the equivalent core approximation and thus to compute directly the surface segregation energy in the presence of adsorbates, and to compare it to that calculated for clean surfaces. This is the subject of the present work.

3. Calculation of the Surface Segregation Energy of an Impurity in the Presence of Adsorbates

We consider a semi-infinite crystal of tungsten, delimited by a (110)-surface, with a single oxygen atom or a whole $p(2 \times 1)$ layer of oxygen atoms on the surface. Our aim is to calculate the change $\Delta^{S'S}$ of SCLS of the atoms of the first layer of W which are directly bound to some oxygen atoms. In the equivalent core approximation $\Delta^{S'S}$ reduces to the variation of the surface segregation energy of a rhenium impurity in the presence and in the absence of the adsorbates in its vicinity. The computation is performed in the tight-binding approximation following the same method as already used in the case of a clean surface [4].

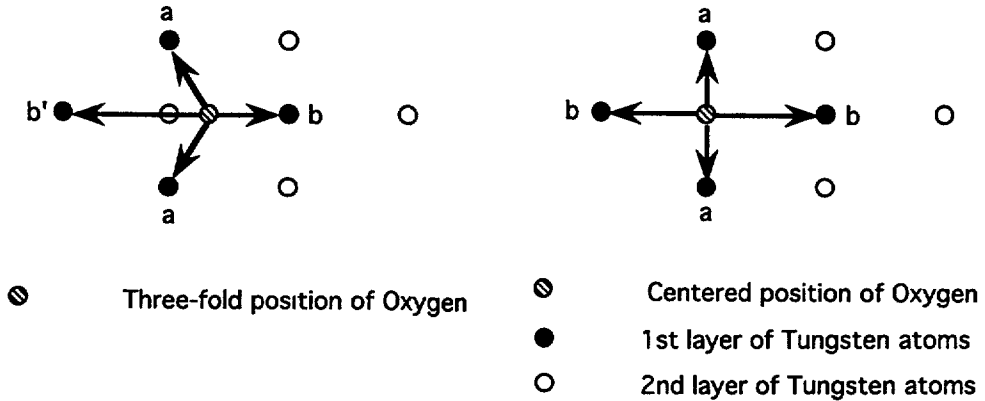


Fig. 1. — Three-fold and centered adsorption sites of an oxygen atom on a (110)W surface.

We assume that the repulsive energy between two neighboring atoms is the same for a W-Re (O-Re) pair as for a W-W (O-W) pair. The segregation energy of Re is then only due to the variation of the band energy contribution when the Re atom, initially in the bulk, is interchanged with a W surface atom, i.e.:

$$E_{\text{segr}} = \int_{-\infty}^{E_f} E \Delta n(E) dE - \Delta E_{\text{Coulomb}} \tag{4}$$

where $\Delta n(E)$ is the variation of the total density of states and $\Delta E_{\text{Coulomb}}$ avoids the double counting of Coulomb energies in the first term.

The density of states is computed from a tight-binding Hamiltonian with a basis set made of 2p valence orbitals for oxygen atoms and restricted to 5d valence orbitals for W and Re atoms, since it is known that in these metals the cohesive properties are largely dominated by d electrons. In this basis, the hopping integrals are calculated using Slater and Koster tables [8] from the parameters $dd\sigma$, $dd\pi$ and $dd\delta$ (for the W-W and W-Re interactions, which are limited to the first and second nearest neighbours) and $pd\sigma$, $pd\pi$ (for the O-W and O-Re interactions, which are limited to the four nearest neighbours of oxygen, cf. Fig. 1). These parameters and their variation with interatomic distance have been given elsewhere [7].

The atomic levels, which are taken as energy zero for W bulk atoms, are modified in the vicinity of the surface and of the impurity due to charge rearrangements. They are determined by requiring the local charge neutrality of each atom in the system.

If we introduce the local density of states (LDOS) on each atom l , $n_l(E)$ (normalized to unity), the segregation energy can be rewritten as :

$$E_{\text{segr}} = \sum_l \Delta E_l = \sum_l \left(L_l \int_{-\infty}^{E_f} E \Delta n_l(E) dE - N_l \Delta(\delta V_l) \right) \tag{5}$$

where L_l is the number of atomic spin-orbitals centered at atom l ($L_l = 10$ for W or Re, $L_l = 6$ for O), $\Delta n_l(E)$ is the perturbation of the LDOS of atom l due to the interchange of a W surface atom with the Re bulk impurity. For an oxygen atom, N_l is the number of 2p electrons ($N_l = 4$) and for a tungsten or rhenium atom, N_l is the number of electrons per atom in the 5d band. In our previous study on SCLS of clean W surfaces [4], the best agreement between surface segregation energies of Re in a W matrix and measured SCLS was obtained

with $N_l(W) = 4.4 e^-/\text{atom}$ and $N_l(\text{Re}) = 5.5 e^-/\text{atom}$. Consequently, we have adopted the same values in this work. Finally $\Delta(\delta V_l)$ is the perturbation of the atomic level δV_l of atom l , the latter being determined, for each configuration, from the set of coupled equations :

$$L_l \int_{-\infty}^{E_f} n_l(E, \delta V_1, \dots, \delta V_l, \dots) dE = N_l \quad (6)$$

The determination of the LDOS, $n_l(E)$, is carried out using a continued fraction expansion with eight exact levels [9].

In practice, the impurity modifies the electronic structure of the host only within a small distance, therefore the summation in equation (5) can be limited to two clusters of atoms around the sites successively occupied by the impurity.

4. Modification of SCLS of W(110) in the Presence of Adsorbed Oxygen

In order to determine the change of SCLS of W(110) in the presence of adsorbed oxygen, we have performed the calculation of the segregation energy, E_{segr} , of a Re atom from the bulk to the (110) surface of W and subtracted the results, obtained for the clean surface, using the same model [4]. Two limits have been considered: a $p(2 \times 1)$ layer of oxygen atoms (coverage $\theta = 1/2$) and an isolated oxygen atom ($\theta \rightarrow 0$).

Let us first discuss the atomic structure of the system. The best fit to intensity *versus* voltage (I-V) curves in low energy electron diffraction (LEED) experiments on the $p(2 \times 1)$ O/W(110) system has been obtained with the oxygen atoms at the three-fold sites [10] (Fig. 1). At this location, the oxygen atoms sit equidistantly above three W atoms. However, when the oxygen atoms are assumed to be at the center of a rhombus of surface atoms, the agreement between theoretical and experimental (I-V) curves is only slightly less satisfactory so that this adsorption site can not be totally excluded, as well as some intermediate position. For both adsorption sites, the interlayer spacing between oxygen and tungsten is found to be 1.25 Å, which corresponds to a bond length O-W of 2.08 Å at the three-fold sites. Moreover, it was found in a previous calculation of the adsorption energy of an isolated oxygen atom on W(110) that the most stable site was actually intermediate between the three-fold and centered sites but closer to the former [11].

In the following we present in detail the results obtained for the three-fold adsorption site at the same distance from the surface (1.25 Å) for both coverages ($\theta = 1/2$, $\theta \rightarrow 0$). The sensitivity of the results to lateral displacements towards the centered site will be discussed in Section 5. We only calculate SCLS on surface atoms which are directly bound (i.e., by a non-vanishing hopping integral) to an oxygen atom since these atoms are expected to be the most perturbed. The surface segregation energy of a Re impurity in W is obtained from the energy difference between a configuration \mathcal{A} , in which a W surface atom near an oxygen atom is replaced by a Re impurity, and a configuration \mathcal{B} , in which a W bulk atom is replaced by a Re atom (Fig. 2). Around the two sites that can be occupied by the Re atom, we define a cluster of atoms (C_{bulk} in the bulk, C_{surf} at the surface) which are significantly perturbed by the presence of the impurity.

From equation (5), the calculation of E_{segr} requires the knowledge of the LDOS at each atom in the clusters C_{bulk} and C_{surf} with and without the Re impurity. The determination of the LDOS of the atoms belonging to cluster C_{bulk} are completely independent from the surface and adsorbate(s) atomic arrangement. Thus, this calculation is carried out once for all. In practice, the cluster C_{bulk} contains the central atom and its first and second nearest neighbours while the cluster C_{surf} must be adapted to each possible atomic arrangement of the adsorbate(s) and of the Re impurity with respect to the W surface.

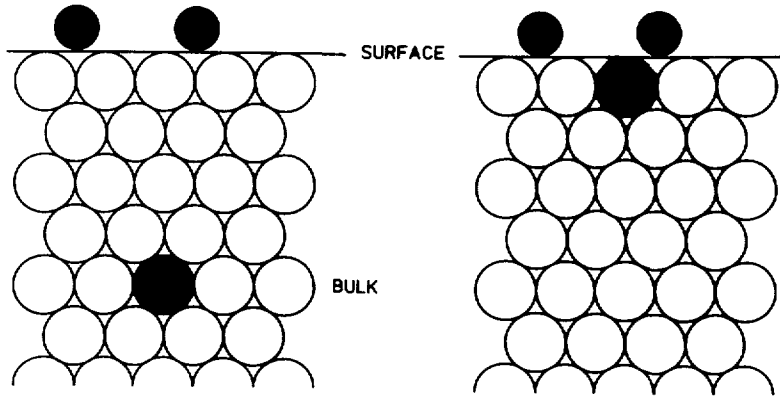


Fig. 2. — Pictorial representation of the two configurations involved in the calculation of surface segregation energies. (●): O atoms; (○): W atoms; (●): Re atoms.

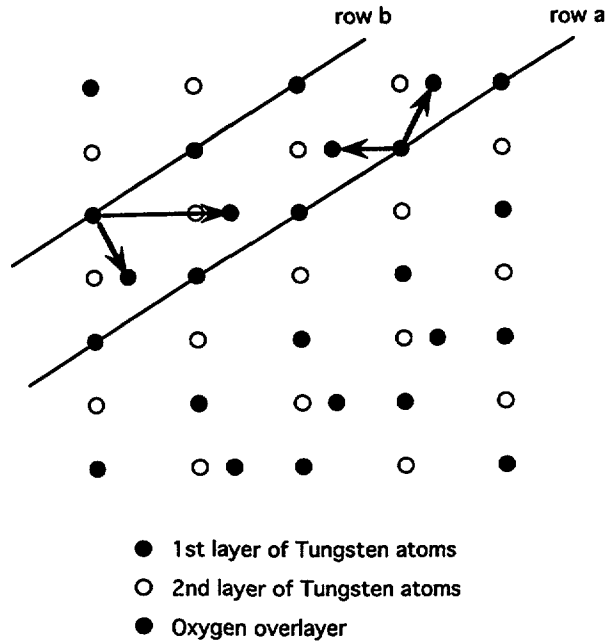


Fig. 3. — Structure of a $p(2 \times 1)$ oxygen overlayer on a $(110)W$ surface.

4.1. $p(2 \times 1)$ OXYGEN OVERLAYER. — The $p(2 \times 1)$ structure is shown in Figure 3. Since the system has a translational symmetry, all the oxygen atoms have the same effective atomic level. On the contrary, on the surface (and in the sublayers) two geometrically inequivalent atomic rows, labelled *a* and *b*, can be distinguished which have different effective atomic levels, perturbed from the bulk one. However, beyond the second layer, calculations show that this perturbation is vanishingly small.

Then a W surface atom is replaced by a Re impurity either in row *a* or in row *b* and, in both

Table I. — Change $\Delta^{S'S}$ of SCLS of W(110) in the presence of a $p(2 \times 1)$ oxygen overlayer deduced from E_{segr} and from the microscopic model. For the labelling of atomic rows, see Figure 3. The oxygen atoms are at three-fold sites and the band filling of W is $N_1(W) = 4.4 e^-/\text{atom}$.

Atomic rows	a (meV)	b (meV)
$\Delta^{S'S}$ from E_{segr}	380	250
$\Delta^{S'S}$ (micr. mod.)	240	200

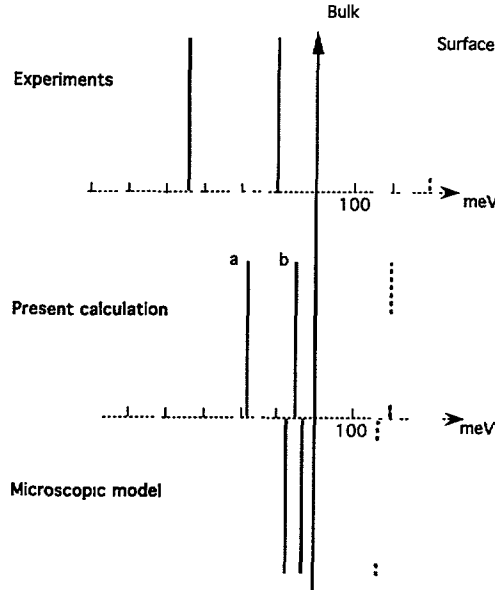


Fig. 4. — Theoretical positions of the core level lines of W(110) in the presence of a $p(2 \times 1)$ oxygen overlayer compared with experiments [12]. a and b refer to the atomic rows shown in Figure 3. The clean surface line (dashed) is shown for comparison but does not appear in the experimental spectrum when the $p(2 \times 1)$ is complete.

cases, the cluster C_{surf} includes all the atoms which are directly bound to the impurity.

The modifications of SCLS due to the presence of oxygen deduced from surface segregation energies together with the predictions of the microscopic model are given in Table I. It can be seen in Figure 4 that, even though the calculated $\Delta^{S'S}$ remain underestimated, the present method significantly improves the agreement with experiments.

4.2. ISOLATED OXYGEN ATOM. — The oxygen atom is directly bound to four W atoms, two of them being geometrically equivalent (Fig. 1). Thus we expect that the presence of an isolated oxygen adatom on the surface will induce three core level lines in the spectrum, due to the excitation of atoms a , b , b' (Fig. 1). Therefore we consider these three positions for the Re impurity. In all cases, the cluster C_{surf} includes all the atoms that are directly bound either to the adatom or to the impurity.

The calculation is carried out as follows. First, it is performed on a clean surface. This gives,

Table II. — Change $\Delta^{S'S}$ of SCLS of W atoms which are neighbours of an isolated oxygen adatom on a (110)W surface deduced from E_{segr} and from the microscopic model. For the labelling of the sites occupied by the core ionized atom, see Figure 1. The oxygen atom is at a three-fold site and the band filling of W is $N_i(W) = 4.4 e^-/\text{atom}$.

Site of the core ionized atom	a (meV)	b (meV)	b' (meV)
$\Delta^{S'S}$ from E_{segr}	320	190	10
$\Delta^{S'S}$ (micr. mod.)	220	100	20

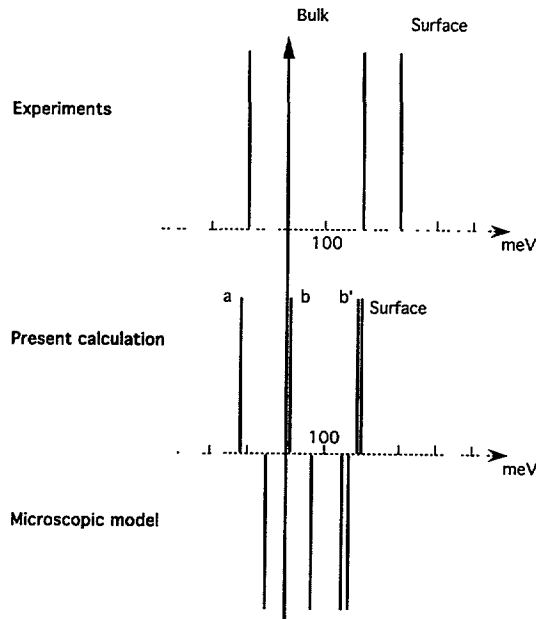


Fig. 5. — Theoretical positions of the core level lines of W(110) in the presence of an isolated oxygen adatom compared with experiments [12]. a , b and b' refer to the sites shown in Figure 1.

in particular, the surface effective atomic levels. Then the system “isolated oxygen+pure W surface” is investigated. (The same calculation is repeated for a Re surface, assumed to be (110) bcc, in order to get the band contribution to the oxygen adsorption energy, which allows the estimation of $\Delta^{S'S}$ by means of Eq. (3)). Finally we replace a surface W atom at sites a , b or b' by a Re impurity.

The results of the present calculation and of the microscopic model are given in Table II. The thermodynamical model predicts an average value of $\Delta^{S'S}$ which almost compensates for the SCLS on the clean surface: i.e., the center of gravity of the core level lines due to the excitation of W atoms near oxygen should be close to the bulk one.

Let us now compare the results of Table II with experimental data (Fig. 5). In both approaches, the highest (lowest) core level binding energy is obtained for the W atom at site a (b') therefore it should correspond to the core level line observed at a higher (lower) binding energy than that of the bulk line. Furthermore, from the surface segregation energy calculations, it is

Table III. — Influence of a lateral displacement of the adsorption site of oxygen from the three-fold site towards the centered site (d is the distance between these two sites) on the change $\Delta^{S'S}$ of SCLS of W atoms directly bound to oxygen adatom(s) : a) $p(2 \times 1)$ overlayer; b) isolated oxygen adatom. For the labelling of atomic rows and sites, see Figure 3 and 1, respectively. The band filling of W is $4.4e^-/\text{atom}$. The SCLS are deduced from surface segregation energies.

a)

Displacement	Atomic row a (meV)	Atomic row b (meV)
0	380	250
$d/4$	370	280
$d/2$	360	310
$3d/4$	350	330
d	340	340

b)

Displacement	Site a (meV)	Site b (meV)	Site b' (meV)
0	320	190	10
$d/4$	340	160	30
$d/2$	370	140	50
$3d/4$	380	130	80
d	390	110	110

expected that the core line corresponding to the W atom at site b should coincide with the bulk line. Finally a glance at Figure 5 shows that the overall agreement with experiments is significantly improved by deducing SCLS from surface segregation energies.

5. Discussion and Conclusions

First of all, we must note that our present interpretation of the core level spectra at low oxygen coverage differs from the assignment given in a previous work using the microscopic model [12] in which the oxygen induced core level line at a binding energy lower than the bulk one was attributed to a W atom at site b instead of b' .

Let us discuss the possible influence of the choice of the parameters entering in the calculations. First, the results presented above have been obtained with $N_l(W) = 4.4e^-/\text{atom}$, which, as already stated, is also the value which gave the best overall agreement between theoretical and experimental SCLS for various W clean surfaces when SCLS are calculated from surface segregation energies [4] and is consistent with the occurrence of the W(100) reconstruction [13]. We have checked the sensitivity of these results to $N_l(W)$ by changing this parameter by $\pm 0.2e^-/\text{atom}$. We have found that the numerical value of $\Delta^{S'S}$ does not change by more than ~ 30 meV and is thus less sensitive to this variation than the SCLS of the clean surface [4]. Furthermore $N_l(W) = 4.4e^-/\text{atom}$ leads to the best fit with experiments. Then, we have verified that the final results of our calculation are only slightly modified (i.e., by a few meV) by increasing the size of the considered clusters C_{bulk} and C_{surf} . Another difficulty comes from the d band limits (which fix the termination of the continued fraction) that have been kept at their bulk value for any coverage whereas we find localised electron states out of the d band, induced by the presence of oxygen. Such an assumption is physically correct when $\theta \rightarrow 0$, but in the case of the $p(2 \times 1)$ overlayer these states give rise to surface bands as a result

of the indirect interaction between oxygen atoms. This can be taken into account by changing slightly the termination of the continued fraction but it brings only very small changes to our results.

As already mentioned in Section 4, the adsorption site may be somewhat displaced from the ternary site towards the centered site. Consequently, we have repeated the calculations for various values of this displacement. We have found that the best agreement with experimental data is obtained for a displacement equal to $d/4$ where d is the distance between ternary and centered positions (Table III).

Finally all calculations have been performed assuming a strict local charge neutrality condition. Indeed, according to [10] the electronic transfer towards oxygen in the $p(2 \times 1)$ overlayer is very small ($\simeq 4.10^{-2} e^-$). Such a charge transfer can be included in our model. The principle of the calculation is unchanged except that a new term $\sum_l \left(-\Delta N_l \Delta(\delta V_l)/2 \right)$ should be added in the right hand side of equation (5) where ΔN_l is the net charge of atom l [14]. Assuming that the charge transfer is the same when replacing a W atom by a Re atom, we have checked that such a charge transfer does not change significantly our results.

In conclusion, the calculation of SCLS from surface segregation energies leads to a better agreement between theoretical and experimental spectra than the microscopic model as well for adsorbate covered W surfaces, especially at low coverage, as for clean W surfaces. Thus, it can be stated that final state effects cannot be neglected in the calculation of surface core level binding energy shifts.

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